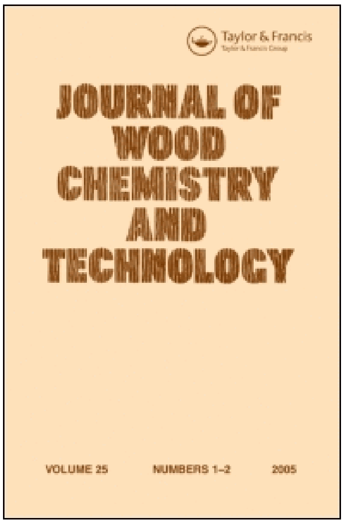

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A Novel Method for Enhanced Recovery of Lignin from Aqueous Process Streams

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Abstract: This study demonstrates that acid precipitation of lignin in the presence of magnetite followed by an applied magnetic field provides a simple method for enhanced lignin recovery from an aqueous stream. The extraction procedure was shown to be sensitive to the relative charge of magnetite and solution pH. Under optimized conditions, 93 wt.% of the softwood lignin from a kraft cooking liquor could be recovered employing this novel separation approach.

Keywords: Lignin, isolation, agglomeration, magnetic separation, magnetite

INTRODUCTION

Lignin is the second most abundant biopolymer on earth after cellulose and has been a unique natural resource throughout history. As issues of sustainability and the biorefinery proceed, greater attention has recently focused at

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developing new applications for lignin beyond its historic usage for energy, surfactants, dispersants, and binders.[1,2] New potential applications of lignin include its use as a co-polymer, resin, anti-oxidant, and a resource for carbon fibers.[3–5] The predominant source of industrial lignin is the kraft pulping process in which wood chips are treated with Na_2S and NaOH at elevated temperatures.[6] This cooking process degrades and solubilizes lignin liberating cellulosic fibers. The spent cooking liquors are concentrated and burned in a recovery furnace to recover the cooking chemicals and energy. The recovery of lignin from cooking liquors has become an active field of study as a source of value-added green chemicals and to enhance production capabilities of a modern pulp mill.[7] A variety of different methods have been explored to recover lignin from cooking liquors including ultrafiltration,[8] organic solvent extraction,[9] acid precipitation[10–12] and precipitation with calcium or polymeric additives.[13,14]

In addition, recent developments in cellulosic ethanol will only serve to increase the amounts of lignin available on a global basis.[15] The conversion of cellulose and hemicelluloses to ethanol will yield a significant process stream of lignin. Although portions of this lignin will be used for biopower generation required for the generation and separation of ethanol, all biorefinery calculations suggest that an excess of lignin will be present beyond the energy requirements of the biorefinery.[16] These future considerations have renewed interests in the isolation and conversion of lignin to value-added chemicals.[17–19]

In light of these needs, the concentration and separation of lignin remains an important research challenge that is relevant to today's chemical pulp mill and future second generation biorefineries. In many of these extraction procedures, the filtration of precipitated lignin from the aqueous solution is an important and difficult component in the overall isolation and processing of lignin. Alternative methods of isolating lignin remains an active field of investigation and this report summarizes our recent efforts at utilizing a combined acidic precipitation onto magnetite, followed by magnetic separation.

EXPERIMENTAL

Chemicals and Materials

All chemical reagents were commercially purchased and used as received. A solution of softwood (SW) cooking liquor (pH: 12.9; 14.4 wt.% solids) was acquired from a commercial kraft pulp mill operating in the southeastern U.S.A.

Magnetic Separation

A commercial SW kraft cooking liquor solution was diluted with nano-pure water yielding a 5.6 wt.% solids solution with a pH of 10.2. A 0.1–1.6%

mass charge of magnetite, based on mass black liquor solids, was then added to the dissolved cooking liquor solutions and stirred for 30 min. The solution pH was adjusted to a specified value by the dropwise addition of 1.00 N sulfuric acid. The solution was then mixed at 100 rpm with a mechanical stirrer for 30 min. The resulting colloidal suspension was then exposed to a 0.80 Tesla static magnetic field and removed from the solution.

Lignin Measurement

Lignin content was measured with a Perkin-Elmer Lambda 900 UV/Vis spectrometer according to modified literature methods.[20] In brief, the black liquor solution was adjusted to pH 10.2. The diluted black liquor solution was then transferred to a quartz curvette. The UV light absorption was determined in 200 to 400 nm range in the double-beam Lambda spectrophotometer. The maximum absorbance at the 280 nm was observed. Lignin concentration was calculated based on a calibration curve established with a series of lignin solution with differing concentrations.

RESULTS AND DISCUSSION

Magnetic separation is a broad field of study with diverse applications including removal of magnetic impurities from process streams,[21] separation of biological systems tagged with paramagnetic micron/nano particles,[22] water purification[23] and deinking of office wastepaper.[24] The key to several of these applications is the agglomeration of materials on magnetite particles and their selective removal with a magnetic field.

Table 1 summarizes our initial studies to evaluate the potential of precipitating lignin in the presence of magnetite followed by magnetic removal at decreasing pH values. These results indicate that the addition of a 0.20 wt.% charge of magnetite to the lignin solution resulted in only a 0.20 wt.% removal

Table 1. Effect of pH on agglomeration and magnetic separation of lignin from kraft cooking liquor containing 0.20 wt.% magnetite

Solution pH	Lignin removal[a] (wt.%)
1.2	49.0
2.2	44.2
3.2	38.9
4.2	4.5
5.2	0.2

[a] Determined by UV analysis.

Table 2. Effect of magnetite charge on magnetic separation of lignin from kraft cooking liquor at pH 1.2

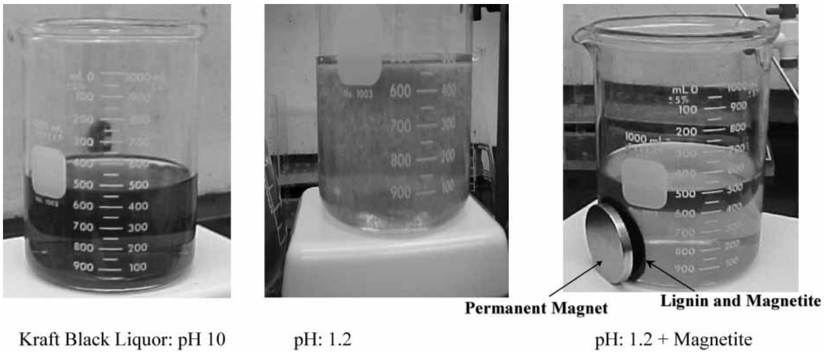
Charge magnetite (wt.%)	Lignin removal (wt.%)	Net lignin removal by magnetite (wt.%)
Original	—	—
0	67.8[a]	—
0.05	71.5	3.6
0.2	74.0	6.2
0.4	74.2	6.4
0.6	75.6	7.8
0.8	91.4	23.6
1.0	93.2	25.4

[a] By sedimentation-decantation.

of the lignin at pH 5.2. However, as the pH of the solution was decreased to 1.2, up to 49.0 wt.% of the lignin could be removed from the solution.

The effect of varying the charge of magnetite on the overall lignin separation process at pH 1.2 was further investigated and these results are summarized in Table 2.

These results clearly demonstrated that at a pH of 1.2, the magnetic removal of lignin was dependent on the magnetite charge. With a 1.0 wt.% charge, about 93 wt.% of the lignin could be removed from solution. Simple pH adjustment of a kraft lignin solution to pH 1.2 followed by sedimentation for 30 min and decanting the aqueous phase provided an ~68 wt.% recovery of lignin. Hence, the addition of magnetite and application of a magnetic field provided another ~25 wt.% recovery of lignin. In addition, as shown in Figure 1, the recovery of lignin agglomerated on magnetite is simple and direct.



Kraft Black Liquor: pH 10

pH: 1.2

pH: 1.2 + Magnetite

Figure 1. Magnetic separation of lignin precipitated on 1.0 wt.% magnetite.

The recovery of lignin from the magnetite can be readily accomplished by dissolution in an organic solvent. For example, the agglomerated lignin-magnetite (see Table 2 with 1.0 wt.% magnetite charge), isolated with a magnetic field, can be readily transferred into DMSO or an ionic liquid,[25] such as 1,3-dimethylimidazolium methylsulfate ([mmim][SO_4Me]). The mixture was stirred and applied with a magnetic field. The DMSO washed magnetite was then recovered and all of the dissolved lignin remained in the organic solvent. Currently, we recover +98% of the magnetite with some loss due to the use of a permanent magnet where it is difficult to remove all magnetite, the use of a switchable electromagnetic may address this and is currently being examined.

CONCLUSIONS

In summary, these results present a new technological approach to remove degraded lignin from dilute kraft pulping liquors. Once removed from the pulping liquor, this lignin could be readily re-dissolved in an organic solvent. A simple application with a magnetic field could be used to recycle the added magnetite for subsequent magnetic lignin separations. Future work will focus on the further optimization of this simple and direct method of recovering lignin to improve the overall efficiency of the process.

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